

Action of Nitrous Acid on Borazaro Compounds

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Diazotisation of borazaro compounds with subsequent treatment with base (sodium acetate) gives boron-free products. Two different reaction paths have been recognised for this reaction: The first leads to the corresponding 1,2-diaza compounds by electrophilic displacement of the boronic acid group by the diazonium ion, the second to a product with twice its molecular weight. Which of the two paths is followed seems to depend on the borazaro compound and the reaction medium employed. Thus when diazotisation is carried out in acetic acid/hydrochloric acid, 10-methoxy-10,9-borazarophenanthrene gives the path 1 product exclusively; 6-methoxy-6,5-borazarobenz[a]anthracene and 5-methoxy-5,6-borazarobenz[a]anthracene give the path 1 product in 50% yield. Under the same conditions 6-methoxy-6,5-borazarochysene gives only the path 2 product.

The synthesis of halogeno compounds will be described, which have been prepared to obtain information about the factors which determine the course of the reaction and the structure of the path 2 reaction product.

 $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$: Inorganic Aromatic Species

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$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ are extremely stable species with a derivative chemistry of sufficient scope to rival that of organic aromatic systems. $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ form stable conjugate acids of somewhat greater strength than sulfuric acid, and are not readily degraded by base. Derivatives containing the following substituents directly on boron, either singly or in combination, have been prepared: halogen, COOH, CN, COOEt, CONH₂, COR, R, NH₂, NCO, N₃, OH, OR, OCOR, SH, carbon monoxide, nitrogen, organic sulfides, amines, nitriles, and amides. Specific examples include: $B_{12}H_{10}(COOH)_2^{-2}$, $B_{10}H_8(NCO)_2^{-2}$, $B_{10}Cl_8(N_2)_2$, $B_{10}H_8(CO)_2$ and $B_{10}H_9COC_6H_5^{-2}$. Synthetic methods and properties will be described, together with observations on stereochemistry, isomer formation and separation, directive effects of substituents and inferences on possible mechanisms of substitution.